

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C08F 14/18</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/21697</b> <b>(43) International Publication Date:</b> 29 September 1994 (29.09.94)
<b>(21) International Application Number:</b> PCT/US94/00833 <b>(22) International Filing Date:</b> 24 January 1994 (24.01.94) <b>(30) Priority Data:</b> 08/036,073 23 March 1993 (23.03.93) US <b>(71) Applicant:</b> MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). <b>(72) Inventor:</b> GROOTAERT, Werner, M., A.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). <b>(74) Agents:</b> BRINK, Robert, H. et al.; Office of Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		<b>(81) Designated States:</b> AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> FLUORINE-CONTAINING POLYMERS AND PREPARATION AND USE THEREOF		
<b>(57) Abstract</b>  Fluoroalkyl sulfates were synthesized and used as a source of fluoroalkyl radicals in aqueous emulsion polymerization. The resulting polymers contained a high level of perfluoroalkyl end groups. When fluoroalkyl disulfates were utilized, the fluoroalkyl moiety was incorporated in the polymer backbone. These disulfates act as monomers, yielding fluoropolymers with specific micro structural fragments, derived from the parent perfluoro disulfate. Novel fluoropolymers can thus be prepared.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

FLUORINE-CONTAINING POLYMERS AND PREPARATION  
AND USE THEREOF

5

This invention relates to fluorine-containing polymers, their preparation and use. In another aspect, this invention relates to methods of free-radical polymerization of ethylenically unsaturated monomers, and to the resulting polymers and shaped articles thereof.

Fluorine-containing polymers, or fluoropolymers, are an important class of polymers and include for example, fluoroelastomers and fluoroplastics. Within this class are polymers of high thermal stability and usefulness at high temperatures, and extreme toughness and flexibility at very low temperatures. Many of these polymers are almost totally insoluble in a wide variety of organic solvents, and are chemically inert. Some have extremely low dielectric loss and high dielectric-strength, and most have unique nonadhesive and low-friction properties. See, for example, F.W. Billmeyer, Textbook of Polymer Science, 3rd ed., pp 398-403, John Wiley & Sons, New York (1984).

Fluoroelastomers, particularly the copolymers of vinylidene fluoride with other ethylenically unsaturated halogenated monomers, such as hexafluoropropene, have particular utility in high temperature applications, such as seals, gaskets, and linings - see, for example, Brullo, R.A., "Fluoroelastomer Rubber for Automotive Applications," Automotive Elastomer & Design, June 1985, "Fluoroelastomer Seal Up Automotive Future," Materials Engineering, October 1988, and "Fluorinated Elastomers," Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 8, pp. 500-515 (3rd ed., John Wiley & Sons, 1979).

Fluoroplastics, particularly polychlorotrifluoroethylene, polytetrafluoroethylene, copolymers of tetrafluoroethylene and hexafluoropropylene, and poly(vinylidene fluoride),  
5 have numerous electrical, mechanical, and chemical applications. Fluoroplastics are useful, for example, in wire, electrical components, seals, solid and lined pipes, and pyroelectric detectors.  
Polychlorotrifluoroethylene is compatible with liquid  
10 oxygen, and remains tough at cryogenic temperatures. See, for example, "Organic Fluorine Compounds," Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 11, pp. 20, 21, 32, 33, 40, 41, 48, 50, 52, 62, 70, 71, John Wiley & Sons, (1980).  
15 Fluorine-containing polymers can be prepared by free-radical initiated polymerization of one or more fluorine-containing ethylenically unsaturated monomers. Free radicals are typically formed by the decomposition of a free-radical initiator. Free-radical initiators  
20 may be decomposed by light, heat, high energy radiation, or as a result of oxidation-reduction reactions. When free radicals are generated in the presence of free-radical polymerizable ethylenically unsaturated monomers, a chain reaction occurs producing  
25 polymer. The polymer can be prepared by polymerization of monomers in bulk, in solution, in emulsion, or in suspension. Fluoroelastomers and fluoroplastics are preferably prepared by aqueous emulsion or suspension polymerization because of the rapid and nearly complete  
30 conversion of monomers, easy removal of the heat of polymerization and ready isolation of the polymer. Emulsion or suspension polymerization typically involves polymerizing monomers in an aqueous medium in the presence of an inorganic free-radical initiator  
35 system, and surfactant or suspending agent.

Polymers of low molecular weight can be prepared by polymerizing monomers in the presence of a chain-transfer agent. Chain-transfer agents react with the

growing polymer chain. In this reaction, the growing polymer chain is terminated and the chain-transfer agent is converted into a radical. This newly-formed free-radical typically can react immediately with  
5 monomer, thereby initiating the polymerization of a new polymer chain. Examples of conventional chain-transfer agents are carbon tetrachloride, acetone, diethyl malonate, and dodecylmercaptan. Chain-transfer activity varies greatly with changes in solvents and  
10 monomers.

In aqueous emulsion or suspension polymerization of fluorine-containing ethylenically unsaturated monomer, conventional chain-transfer agents generally can terminate a growing polymer chain but generally do  
15 not immediately react with monomer to initiate a new polymerization. As a result, the polymerization generally is slow and most polymer chains contain an ionic end-group due to initiation by ionic radical-initiator, e.g., sulfate radical ion.

20 Ionic or polar end-groups generally are not desirable because of detrimental affects on rheology. U.S. Pat. No. 4,524,197 (Khan) states that the presence of acid end-groups detrimentally effects the processing characteristics of fluoroelastomers since these groups  
25 increase the viscosity of the polymer and interfere with curing systems, especially those based on quaternary phosphonium salts.

Ionic or polar end-groups may also reduce the thermal stability of certain fluorine-containing  
30 polymers. U.S. Pat. No. 4,743,658 (Imbalzano et al.) states that perfluorinated resins with certain end groups, especially -COF, -CONH<sub>2</sub>, and -CF<sub>2</sub>CH<sub>2</sub>OH, can be chemically reactive and thermally unstable. Such end groups can evolve HF, which is generated by the  
35 oxidation, hydrolysis, and/or thermal decomposition of these end groups.

Polymers with non-ionic end groups can be prepared by the use of non-ionic free-radical initiators, e.g.,

azobisisobutyronitrile or benzoyl peroxide. However, most non-ionic free-radical initiators are generally insoluble in water and are therefore not suitable for aqueous emulsion or suspension polymerization. The  
5 employment of water-insoluble initiators would require the use of organic co-solvents and/or seed lattices produced with water-soluble initiators.

Chang-Ming Hu, Feng-Ling Quing, and Wei-Yuan Huang, J. Org. Chem., 1991, 55, 2801-2804, reported  
10 that perfluoroalkyl sulfinates dissolved in an organic solvent such as dimethyl formamide, react smoothly with allyl and propargyl halides in the presence of an oxidant, to yield 3-(perfluoroalkyl) prop-1-enes or allenes, respectively, in very good yields. The  
15 mechanism of this reaction is believed to be a free radical addition-elimination reaction.

Because sulfinates are well known electron donors, a suitable electron acceptor (oxidant) should initiate electron transfer from  $R_fSO_2Na$  to generate  $R_fSO_2\cdot$  radicals  
20 and, subsequently,  $R_f\cdot$  radicals. See, for example, Chang-Ming Hu, et al., supra. The oxidants described in Hu's paper, were  $O_2$ ,  $Ce(SO_4)_2$ , and ammonium persulfate. Ammonium persulfate was said to be the preferred reagent with dimethyl formamide (DMF) as the  
25 solvent.

Although it is widely recognized that fluoropolymers with perfluorinated end groups are more thermally stable and show rheological advantages over fluoropolymers with ionic end groups, the only  
30 described ways to get these perfluorinated end groups is by use of fluorinated peroxides as initiators, see e.g., U.S. Pat. Nos 4,654,444 and 4,663,407 (Oka et al.) or by direct fluorination processes on the final polymer, see e.g., European patent application EP  
35 91107750.1, Ihara, et al. and references cited therein.

However, perfluoroperoxides are extremely unstable substances and need to be handled in dilute solutions in halogenated solvents such as Freon™ 113 at low

temperature. Besides the fact that the handling of these substances poses a significant hazard, they also require the use of organic cosolvents (typically Freon™ 113) during the polymerization. The use of Freon™ 113 is undesirable because of possible ozone depletion. Also, because of the thermal instability of these perfluoroperoxides, the polymerization should be carried out below room temperature. This imposes the expense of cooling equipment.

Direct fluorination of the final polymer, to obtain perfluorinated end groups, is a cumbersome process requiring highly reactive fluorine gas to be contacted with finely powdered fluoropolymer at elevated temperatures for several hours. In addition, unless the backbone is perfluorinated, direct fluorination may also fluorinate the backbone which may be undesirable. The degree of fluorination is highly dependant on the polymer particle size, the temperature, the fluorine content of the fluorination gas, and the contact time. These parameters are difficult to control reproducibly. Therefore, it is difficult to obtain a uniform degree of fluorination, especially in a factory environment.

Briefly, in one aspect, the present invention provides a method for the preparation of fluorine-containing polymer comprising polymerizing, under free-radical conditions, an aqueous emulsion or suspension of a polymerizable mixture comprising a fluoroaliphatic-radical containing sulfinat, and an oxidizing agent capable of oxidizing said sulfinat to a sulfonyl radical. Preferably, said oxidizing agent is water soluble. Preferably, said polymerizable mixture comprises fluorine-containing ethylenically-unsaturated monomers.

In another aspect, this invention provides a fluorine-containing polymer comprising a fluoroaliphatic group, e.g., fluoroalkyl or fluoroalkylene group, derived from a fluoroaliphatic-

radical containing sulfinates. The polymer backbone chain can contain heteroatoms, e.g., nitrogen atoms.

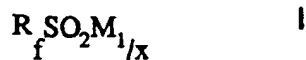
The polymerization method of this invention can be used to rapidly prepare fluorine-containing polymers that are easy to process. Preferred oxidizing agents are persulfates, e.g., ammonium persulfate. High yields of fluorine-containing polymer with perfluorinated end groups were obtained when fluoroaliphatic-radical containing sulfinates were used in combination with ammonium persulfate.

The sulfinates are stable salts that can be stored for several months at room temperature without any appreciable loss of activity. Because sulfinates and persulfates are very soluble in water, they readily react with each other in the aqueous phase of the emulsion or suspension. The resulting perfluoroalkyl radical that is formed from this reaction is hydrophobic and therefore readily collapses or absorbs onto the micelle or the polymer particles, inducing a rapid polymerization.

The majority of the polymer end-groups formed by the method of this invention are fluoroaliphatic, e.g.  $C_nF_{2n+1}$  and, when hydrogen-containing monomers are used, hydride, e.g.  $CF_2H$  and  $CH_3$ . Very small amounts of  $CH_2OH$  (if any) end groups are detected in the final polymer. As used herein, "end-group" refers to groups at the end of the polymer chain or at the end of long or short branches.

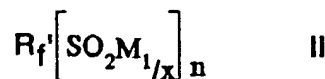
A class of the fluoroaliphatic sulfinates useful in this invention can be represented by the following general formulae





or

5



wherein

- 10  $R_f$  represents a monovalent fluoroaliphatic radical having, for example, from 1 to 20 carbon atoms, preferably 4 to 10 carbon atoms,  $R_f'$  represents a polyvalent, preferably divalent, fluoroaliphatic radical having, for example, from 1 to 20 carbon atoms, 15 preferably from 2 to 10 carbon atoms, M represents a hydrogen atom or cation with valence x, which is 1 to 2, and is preferably 1, n is 1 to 4, preferably 1 or 2.

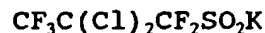
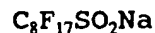
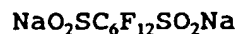
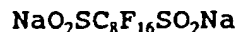
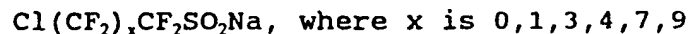
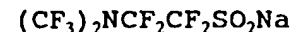
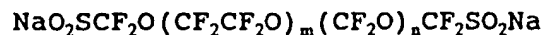
The monovalent fluoroaliphatic radical,  $R_f$ , is a fluorinated, stable, inert, non-polar, saturated 20 moiety. It can be straight chain, branched chain, and, if sufficiently large, cyclic, or combinations thereof, such as alkyl cycloaliphatic radicals. Generally,  $R_f$  will have 1 to 20 carbon atoms, preferably 4 to 10, and will contain 40 to 83 weight percent, preferably 50 to 25 78 weight percent fluorine. The preferred compounds are those in which the  $R_f$  group is fully or substantially completely fluorinated, as in the case where  $R_f$  is perfluoroalkyl,  $C_n F_{2n+1}$ , where n is 1 to 20.

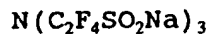
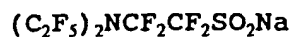
The polyvalent, preferably divalent, 30 fluoroaliphatic radical,  $R_f'$ , is a fluorinated, stable, inert, non-polar, saturated moiety. It can be straight chain, branched chain, and, if sufficiently large, cyclic or combinations thereof, such as alkylcycloaliphatic diradicals. Generally,  $R_f'$ , will 35 have 1 to 20 carbon atoms, preferably 2 to 10. The preferred compounds are those in which the  $R_f'$  group is perfluoroalkylene,  $C_n F_{2n}$ , where n is 1 to 20, or perfluorocycloalkyl,  $C_n F_{2n-2}$ , where n is 5 to 20.

With respect to either  $R_f$  or  $R_f'$ , the skeletal chain of carbon atoms can be interrupted by divalent oxygen, hexavalent sulfur or trivalent nitrogen hetero atoms, each of which is bonded only to carbon atoms, but preferably where such hetero atoms are present, such skeletal chain does not contain more than one said hetero atom for every two carbon atoms. An occasional carbon-bonded hydrogen atom, iodine, bromine, or chlorine atom may be present; where present, however, they preferably are present not more than one for every two carbon atoms in the chain. Where  $R_f$  or  $R_f'$  is or contains a cyclic structure, such structure preferably has 6 ring member atoms, 1 or 2 of which can be said hetero atoms, e.g., oxygen and/or nitrogen. Examples of  $R_f$  radicals are fluorinated alkyl, e.g.,  $C_4F_9-$ ,  $C_6F_{13}-$ ,  $C_8F_{17}-$ , alkoxyalkyl, e.g.,  $C_3F_7OCF_2-$ . Examples of  $R_f'$  are fluorinated alkylene, e.g.,  $-C_4F_8-$ ,  $-C_8F_{16}-$ . Where  $R_f$  is designated as a specific radical, e.g.,  $C_8F_{17}-$ , it should be understood that this radical can represent an average structure of a mixture, e.g.,  $C_6F_{13}-$  to  $C_{10}F_{21}-$ , which mixture can also include branched structures.

Representative fluoroaliphatic sulfinic compounds useful in the practice of this invention include the following:

25

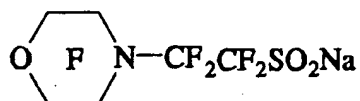
30  $Cl(CF_2)_8OC_2F_4SO_2Na$ 35  $NaO_2SC_2F_4OC_2F_4X$ , where X is Br or I



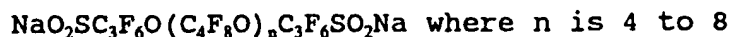
5



10

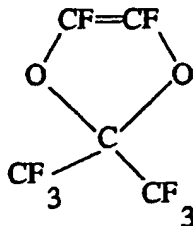


15



Suitable fluorine-containing ethylenically-unsaturated monomers for use in the method of this invention include the terminally unsaturated monoolefins typically used for the preparation of fluorine-containing polymers such as vinylidene fluoride, hexafluoropropene, chlorotrifluoroethylene, 2-chloropentafluoropropene, perfluoroalkyl vinyl ethers, e.g.,  $\text{CF}_3\text{OCF}=\text{CF}_2$  or  $\text{CF}_3\text{CF}_2\text{OCF}=\text{CF}_2$ , tetrafluoroethylene, 1-hydropentafluoropropene, 2-hydropentafluoropropene, dichlorodifluoroethylene, trifluoroethylene, 1,1-dichlorofluoroethylene, vinyl fluoride, and mixtures thereof. Perfluoro-1,3-dioxoles such as

35



may also be used. The perfluoro-1,3-dioxole monomers and their copolymers are described, for example, in U.S. Pat. No. 4,558,141 (Squire). Certain fluorine-containing di-olefins are also useful, such as,  
5 perfluorodiallylether and perfluoro-1,3-butadiene. Said fluorine-containing monomer, or fluoromonomer, may also be copolymerized with fluorine-free terminally unsaturated monoolefin comonomers, e.g., ethylene or propylene. Preferably at least 5% by weight, most  
10 preferably at least 50%, of all monomers in said polymerizable mixture are fluorine-containing. Said fluorine-containing monomer may also be copolymerized with iodine- or bromine-containing cure-site comonomers in order to prepare peroxide curable polymers, e.g.,  
15 fluoroelastomers. Suitable cure-site monomers include terminally unsaturated monoolefins of 2 to 4 carbon atoms such as bromodifluoroethylene, bromotrifluoroethylene, iodotrifluoroethylene, and 4-bromo-3,3,4,4-tetrafluorobutene-1. Preferably, all  
20 or essentially all of the comonomers in said polymerizable mixture are ethylenically unsaturated monomers.

The method of this invention can comprise the use of perfluorosulfinate in otherwise conventional free-  
25 radical polymerization. Such conventional polymerization includes free-radical polymerization of monomers alone or as solutions, emulsions, or dispersions in an organic solvent or water. Polymerization in an aqueous emulsion or suspension is  
30 often preferred because of the rapid and nearly complete conversion of monomers, easy removal of the heat of polymerization, and ready isolation of the polymer. Emulsion or suspension polymerization typically involves polymerizing monomers in an aqueous  
35 medium in the presence of an inorganic free-radical initiator system and surfactant or suspending agent.

In one aspect, the method of this invention comprises the use of fluorinated sulfinate as a

reducing agent and a water soluble oxidizing agent capable of converting the sulfinic acid to a sulfonyl radical. Preferred oxidizing agents are sodium, potassium, and ammonium persulfates, perphosphates, 5 perborates, and percarbonates. Particularly preferred oxidizing agents are sodium, potassium, and ammonium persulfates. The sulfonyl radical so produced is believed to eliminate  $\text{SO}_2$ , forming a fluorinated radical that initiates the polymerization of the ethylenically 10 unsaturated monomers.

In addition to the sulfinic acid, other reducing agents can be present, such as sodium, potassium or ammonium sulfites, bisulfite, metabisulfite, hyposulfite, thiosulfite, phosphite, sodium or 15 potassium formaldehyde sulfoxylate or hypophosphite. Activators such as ferrous, cuprous, and silver salts, may also be present.

Aqueous emulsions can be carried out under conventional steady-state conditions in which, for 20 example, monomers, water, surfactants, buffers and catalysts are fed continuously to a stirred reactor under optimum pressure and temperature conditions while the resulting emulsion or suspension is removed continuously. An alternative technique is batch or 25 semibatch polymerization by feeding the ingredients into a stirred reactor and allowing them to react at a set temperature for a specified length of time or by charging ingredients into the reactor and feeding the monomer into the reactor to maintain a constant 30 pressure until a desired amount of polymer is formed.

The amount of fluoroaliphatic sulfinic acid used can vary, depending, for example, on the molecular weight of polymer desired. Preferably the amount of fluoroaliphatic sulfinic acid is from 0.01 to 50 mole %, 35 and most preferably from 0.05 to 10 mole %, of sulfinic acid compound based on total quantity of monomers.

Combinations of monosulfonates, disulfonates, and trisulfonates can be used, depending on whether it is

desired to use sulfinate as an initiator, a monomer, or both. When polyvalent sulfonates, such as those represented by Formula II, are used, the sulfonate is a monomer and the fluorinated moiety is incorporated into the polymer backbone. When monosulfonates are used the fluorinated moiety is incorporated as a polymer end group.

Polymers prepared by the method of this invention, such as fluoroelastomer gums, can be compounded and cured using conventional methods. Such polymers are often cured by nucleophiles such as diamines or polyhydroxy compounds. For example, the fluoroelastomers of this invention may be crosslinked with aromatic polyhydroxy compounds, such as bisphenols, which are compounded with the polymer along with a curing accelerator, such as a quaternary phosphonium salt, and acid acceptors, such as magnesium oxide and calcium hydroxide. Particularly useful polyhydroxy compounds include 4,4'-thiodiphenol, isopropylidene-bis(4-hydroxybenzene), and hexafluoroisopropylidene-bis(4-hydroxybenzene) ("bisphenol AF") which are described, for example, in U.S. Pat. No. 4,233,421 (Worm). Such crosslinking methods are described, for example, in U.S. Pat. Nos. 4,287,320 (Kolb), 4,882,390 (Grootaert et al.), 5,086,123 (Guenther et al.), and Canadian patent 2056692 (Kruger et al.).

Certain polymers may be cured with peroxides. A cure-site monomer susceptible to free-radical attack is generally required to render polymers peroxide-curable. For example, polymers which contain interpolymerized units derived from iodine- or bromine-containing monomers are often peroxide-curable. Such cure-site monomers are described, for example, in U.S. Pat. Nos. 4,035,565 (Apotheker et al.), 4,450,263 (West), 4,564,662 (Albin), and Canadian Pat. application No. 2,056,692 (Kruger et al.).

The polymers of this invention can also be compounded with processing agents, such as those conventionally used to aid in the molding or extrusion of the formulation, e.g. carnauba wax or

5 dichlorodiphenyl sulfones and other diorgano sulfur oxides, such as those described in U.S. Pat. No. 4,287,320 (Kolb).

Fillers can be mixed with the polymers of this invention to improve molding characteristics and other  
10 properties. When a filler is employed, it can be added in amounts of up to about 100 parts per hundred parts by weight of polymer, preferably between about 15 to 50 parts per hundred parts by weight of the polymer. Examples of fillers which may be used are thermal-grade  
15 carbon blacks, or fillers of relatively low reinforcement characteristics such as clays and barytes.

The sulfinate compounds useful in this invention result in polymers which have non-polar, non-ionic end  
20 groups. These non-ionic end groups generally result in improved properties such as improved thermal stability and improved rheological behavior. Polymers with non-ionic end groups exhibit lower apparent viscosities during processing, e.g. injection molding, when  
25 compared at the same shear rates to polymers with ionic end groups. The resulting polymers may be elastomers or plastics. The polymers may be shaped to form useful articles including O-rings, fuel-line hoses, shaft seals, and wire insulation.

30 When disulfates are used in the polymerization method of this invention, diradicals are formed that are incorporated in the polymer backbone. This method can be used to prepare a variety of new polymers with new microstructures which would otherwise be  
35 inaccessible.

The polymers of this invention can be mixed with other polymers, for example, with polymers of higher or lower molecular weight to give a bimodal molecular-

weight mixture. For example, low molecular-weight polymers of this invention can be mixed with conventional fluorine-containing polymers to improve the processing characteristics thereof.

5

#### EXAMPLES

The cure characteristics and rheological properties of uncured compositions were obtained using ASTM test method D 2084-75 with no preheat, an  
10 oscillator frequency of 100 cpm and a 3' arc, at 177°C. Minimum torque ( $M_L$ ), highest torque attained during a specified period of time when no plateau or maximum torque is obtained ( $M_H$ ), time for torque to increase 0.2 N.m above  $M_L$  ( $t_2$ ), and time for torque to reach  $M_L +$   
15  $0.9 M_H - 0.9 M_L(t_2'(90))$  were determined. The results are shown in Table 2.

Compounded polymer compositions were press-cured for 10 min. at 177°C and post-cured for 16 hours at 230°C and physical properties determined. Tensile  
20 strength at break, elongation at break, and modulus at 100% elongation were obtained using ASTM Method D-412-80 on a sample cut from 1.8 mm sheet of cured polymer with ASTM Die D. Hardness (Shore A-2) was measured at room temperature on cured samples according to ASTM  
25 Method D-2240-81 using Shore Instrument and Mfg. Co. "A-2" hardness measuring device. Compression set was determined using ASTM Method D-395-78, Method B, on cured (10 min. press cure at 177°C followed by 16 hours postcure at 230°C) O-rings after 25% compression for 70  
30 hours at 200°C. Compression set results are reported as percent of the compression remaining.

The following Examples describe the preparation of perfluoroalkyl sulfinates and their use as free radical  
35 monomers to prepare fluoropolymers of the invention containing perfluoroalkyl end groups or perfluoroalkylene chain segments.



### Preparation of sulfinates

The fluorochemical sulfinates  $C_8F_{17}SO_2Na$  and  $(CF_2)_6(SO_2Na)_2$  ("FS-1" and "FS-2") were prepared by deiodosulfination of the corresponding iodides ( $C_8F_{17}I$  and  $I(CF_2)_6I$ ) with  $Na_2S_2O_4$  following the general procedure of Hu et al. in J. Org. Chem., Vol. 56, No. 8, 1991, page 2803.

The fluorochemical sulfinate  $C_4F_9SO_2H$  ("FS-3") was prepared by reduction of the corresponding sulfonyl fluoride  $C_4F_9SO_2F$  with  $Na_2SO_3$ . The purity of these fluorochemical sulfinates, as determined by  $^{19}F$  NMR analysis, was about 90%. (About 9% of  $HCF_2C_7F_{14}SO_2Na$  was present in FS-1.)

Fluorochemical sulfinate N,N-bis (2-sulfinotetrafluoroethyl)perfluoropiperazine ("FS-4"), was prepared by reduction of N,N'-bis[2-(fluorosulfonyl)ethyl] piperazine, m.p. 73°C, with  $NaBH_4$  in tetrahydrofuran (THF) solution. The solid reaction product, obtained on evaporation of the THF, was dissolved in 10% aqueous sulfuric acid and the sulfinic acid product, FS-4, was recovered by extraction with diethyl ether.  $^{19}F$  NMR analysis of the sulfinic acid, m.p. 115°C dec., indicated 97% purity. The N,N'-bis[2-(fluorosulfonyl)ethyl] piperazine was prepared by the addition of 2 moles of vinylsulfonylfluoride to piperazine followed by electrochemical fluorination of the resulting adduct.

### Preparation of polymers

Several fluoropolymers were prepared using the above fluorochemical mono- and disulfinates. Aqueous emulsion polymerization utilizing these sulfinates were carried out with the following monomers: vinylidene fluoride ( $VF_2$ ,  $CH_2=CF_2$ ), hexafluoropropylene (HFP,  $CF_3CF=CF_2$ ), tetrafluoroethylene (TFE,  $CF_2=CF_2$ ), bromodifluoroethylene cure site monomer (BDFE,  $CF_2=CHBr$ ), and chlorotrifluoroethylene (CTFE).

Example 1

A 4-L stainless steel high pressure reactor was charged with 2.8 L of deionized water, 12 g of  $K_2HPO_4$ , 4 g of  $(NH_4)_2S_2O_8$  and 9 g of FS-1 ( $C_8F_{17}SO_2Na$ ). The reactor  
5 was evacuated (vacuum pump) and then pressurized with nitrogen to 0.17 MPa (25 psig). This evacuation and pressurization was repeated four consecutive times. The reactor and contents were then heated to 71°C and pressurized to 0.90 MPa (130 psig) with a mixture of  
10  $VF_2$  (61.7 weight %) and HFP (38.3 weight %). The reactor contents were agitated (650 rpm) and pressure maintained at 0.90 MPa with the monomer mixture as the monomers were consumed in the polymerization reaction. After a period of three hours, during which a total of  
15 860 g of the monomer mixture was used, the reactor was cooled to room temperature.

Excess monomer was vented and the reactor drained. A portion of the white latex (2.5 kg) was added slowly to a solution of 18 g of  $MgCl_2 \cdot 6H_2O$  in 800 g of water  
20 and 25 g of n-butyl alcohol. The white rubbery polymer which precipitated was washed several times with hot deionized water and dried overnight in a circulating air oven at 100-120°C.  $^{19}F$  NMR analysis of the polymer (in perdeutero acetone solution,  $CFCl_3$  reference) showed  
25 resonances at -80.5 ppm ( $CF_3$ ) and -120 to -126 ppm ( $CF_2$ ), supporting the presence of a  $C_8F_{17}$  end group in the polymer. Further analysis showed the presence of (in relative mole %) polymer units derived from 78.37%  $VF_2$ , 20.98% HFP, and the following end groups: 0.10%  
30  $C_8F_{17}$ , 0.46%  $HCF_2$  and 0.09%  $CH_3CF_2$ . A FT IR spectrum of a thick film, revealed no absorptions between 1500 and 2000  $cm^{-1}$ , while a comparative  $VF_2$ /HFP copolymer (C1 above), prepared without the fluorochemical sulfinate, had absorption peaks at 1714 and 1753  $cm^{-1}$  indicating  
35 polar (carbonyl) end groups.

Comparative Example C1

Comparative Example C1 is a copolymer of VF<sub>2</sub> and HFP (about 80/20 mole % ratio) prepared using conventional emulsion polymerization recipes as described in Ex. 1, without fluorochemical sulfinate.

Example 2

The polymerization described in Example 1 was repeated with 1/2 of the quantity of initiators and with the addition of a fluorochemical emulsifier. Thus, 2.8 L of deionized water, 12 g of K<sub>2</sub>HPO<sub>4</sub>, 2 g of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 4.5 g of FS-1 (C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>Na) and 0.6 g of C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)CH<sub>2</sub>COOK emulsifier were charged to the 4 L reactor. Following the same procedure as in Ex. 1, a total of 870 g of monomer mixture was polymerized. The polymerization took five hours and twenty minutes. Analytical data obtained on the resulting polymer supported the presence of C<sub>8</sub>F<sub>17</sub> end groups.

Example 3

The fluorochemical sulfinic acid, FS-3, C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>H, was employed in this polymerization. It was first converted to the sodium salt, C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>Na, by dissolving 5 g of the sulfinic acid in 100 mL deionized water and adding 0.7 g of NaOH followed by 2 g of K<sub>2</sub>HPO<sub>4</sub>. This solution was added to 2.8 L of deionized water containing 10 g of K<sub>2</sub>HPO<sub>4</sub>, 4 g of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 0.6 g of C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)CH<sub>2</sub>COOK emulsifier. The solution was added to the high pressure reactor and 1000 g of the same monomer blend used in Example 1 polymerized at a pressure of 0.79 MPa (115 psig) at 71°C over a period of 4 hours. A portion of the resulting latex (2.0kg) was coagulated and the white, rubbery polymer product isolated, washed and dried as described in Ex 1. The Mooney viscosity of the rubber (ML 1+10 @ 121°C) was 71. <sup>19</sup>F NMR analysis showed resonances at -80.9, -123.9 and -125.5 ppm, supporting the presence of the C<sub>4</sub>F<sub>9</sub> end group in the polymer chains.

Example 4

Example 3 was repeated except that a different monomer mixture was used. 950 g of a monomer mixture from an 8 L high pressure cylinder containing a mixture of 59.4 weight %  $\text{VF}_2$ , 40.3 % HFP and 0.40 % BDFE cure site monomer. The monomer blend was polymerized over a period of 6.5 hours at a pressure of 0.79 MPa (115 psig) at 71° C. A portion of the resulting latex was coagulated and the white polymer product was washed and dried as described in Example 1. The polymer had a Mooney viscosity ((ML 1+10 @ 121°C) of 61.  $^{19}\text{F}$  NMR analysis supported the presence of the  $\text{C}_4\text{F}_9$  end groups in the polymer. The polymer contained 0.18 wt. % bromine as determined by X-ray fluorescence.

15

Example 5

This Example describes the preparation of a fluoropolymer of  $\text{VF}_2$ , HFP and TFE using the sulfinatate FS-1.

20 An 86-L high pressure reactor was charged with deionized water (45 kg),  $\text{K}_2\text{HPO}_4$  (160.7 g),  $\text{C}_8\text{F}_{17}\text{SO}_2\text{Na}$  (143.2 g),  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (64 g) and  $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{CH}_2\text{COOK}$  (9.6 g) emulsifier. After 4 consecutive vacuum and nitrogen purge cycles, the reactor was pressurized to 0.76 MPa (110 psig) at 71°C. with 384 g  $\text{VF}_2$ , 853 g HFP and 175 g of TFE. Agitation (130 rpm) was started and as soon as a pressure drop occurred, the 3 monomers were added at a rate to maintain constant pressure with the following monomer composition: 44.9 wt.%  $\text{VF}_2$ , 31.5% HFP and 23.6% TFE. After a total of 15.76 kg of monomers had reacted, the monomer supply was stopped and the reaction continued until the pressure decreased to 0.43 MPa (61 psig). At this point, the reactor and contents were cooled to room temperature and unreacted monomers vented. The reactor was then drained and the latex polymer product was coagulated and the white, rubbery polymer product washed and dried as described in Ex. 1. The polymer had a Mooney viscosity (ML 1+10 @ 121°C) of

69 and a composition (by  $^{19}\text{F}$  NMR analysis) of polymer units derived from 41.8 wt%  $\text{VF}_2$ , 32.8% HFP and 25.2% TFE, and with 0.23%  $\text{C}_8\text{F}_{17}$  end groups.

#### 5 Example 6

This Example describes the preparation of a fluoropolymer of  $\text{VF}_2$  and HFP using a disulfinate as an initiator.

To a 4 L stainless steel high pressure reactor was charged 2.8 L deionized water, 12 g of  $\text{K}_2\text{HPO}_4$  and 2 g of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . The reactor was evacuated and the vacuum broken with nitrogen, and this cycle repeated 4 times. Then a solution of 4.2 g of the fluorochemical disulfinate FS-2,  $(\text{CF}_2)_6(\text{SO}_2\text{Na})_2$ , in 100 mL water was charged together with a solution of 0.6 g of  $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{CH}_2\text{COOK}$  emulsifier in 100 mL of water. The reactor was pressurized to 0.90 MPa (130 psig) at  $71^\circ\text{C}$  with a monomer blend of 61.7 wt.%  $\text{VF}_2$  and 38.3% HFP. The reactor contents were stirred (600 rpm) and the polymerization continued for 6 hours until a total of 360 g of monomers was polymerized. The resulting polymer latex was coagulated and the white, rubbery polymer product washed and dried as described in Ex. 1 A  $^{19}\text{F}$  NMR analysis showed resonances in the region -119 to -123 ppm ( $\text{CFCl}_3$  standard) indicative of  $-\text{CF}_2(\text{CF}_2)_x\text{CF}_2-$  units in the polymer backbone, calculated to be a level of about 0.06 mole % of  $-(\text{CF}_2)_6-$  units based on total moles of interpolymerized units.

#### 30 Example 7

This Example describes the preparation of a fluoropolymer of  $\text{VF}_2$  and HFP using another disulfinate as an initiator.

Example 6 was repeated except that in place of the FS-2 sulfinate, 4.9 g of FS-4 was used, after conversion to the sodium salt,  $\text{NaO}_2\text{SC}_2\text{F}_4\text{N}(\text{CF}_2\text{CF}_2)_2\text{NC}_2\text{F}_4\text{SO}_2\text{Na}$ , with aqueous sodium hydroxide. The reactor was pressurized to 0.90 MPa

- (130 psig) at 71°C with a monomer blend of 61.7 wt.% VF<sub>2</sub> and 38.3% HFP. The reactor contents were stirred (600 rpm) and the polymerization continued for 4.5 hours until a total of 780 g of monomers was polymerized.
- 5 The resulting polymer latex was coagulated and the white, rubbery polymer product washed and dried as described in Ex. 1. <sup>19</sup>F NMR analysis (in perdeuterated DMF solvent) showed resonances due to CF<sub>2</sub>-N-CF<sub>2</sub>- at -90.7 ppm supporting the presence of the -
- 10 C<sub>2</sub>F<sub>4</sub>N(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>NC<sub>2</sub>F<sub>4</sub>- unit in the polymer backbone.

#### Example 8

- This Example describes the preparation at room temperature of a fluoroplastic,
- 15 polychlorotrifluoroethylene by the polymerization of chlorotrifluoroethylene (CTFE) in the presence of a fluorochemical sulfinate.

- In a 4 L high pressure reactor was placed 3.44 kg of deionized water, 22.6 g Na<sub>2</sub>HPO<sub>4</sub>, 19.3 g of C<sub>7</sub>F<sub>15</sub>COONH<sub>4</sub>
- 20 emulsifier and 16.0 g of C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>Na. After successive evacuations with a vacuum pump and pressurizing with nitrogen followed by a final evacuation, the reactor contents were stirred at 750 rpm and heated to 27°C at a pressure of 0.0048 MPa (0.7 psig). Then 20.7 g of a
- 25 35 wt. % aqueous solution of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were added concurrently with 1,000 g of CTFE over 3 hours at 26°C. The reactor pressure increased from 0.0048 MPa (0.7 psig) to 0.72 MPa (104 psig) over this period. The reactor was held at a temperature of about 26°C for 62
- 30 hours during which time the pressure fell to 0.12 MPa (17 psig). The reactor was cooled to room temperature and the product, a white emulsion, was drained and freeze-coagulated overnight to yield a flaky, white solid which was collected by aspirator suction on a
- 35 linen cloth and washed 7 times with a 77 wt % water and 23 wt % methanol solution. <sup>19</sup>F NMR analysis supported the presence of C<sub>8</sub>F<sub>17</sub> end groups in the polymer.

### Example 9

This example describes the preparation of a fluoropolymer of VF<sub>2</sub> and HFP at room temperature using a combination of perfluoroalkyl sulfinate (FS-1),

5 C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>Na, and potassium sulfite, K<sub>2</sub>SO<sub>3</sub>, as reducing agents.

To a 4-L high pressure reactor was 2.8 L deionized water, 12 g K<sub>2</sub>HPO<sub>4</sub>, 9 g C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>Na, 0.09 g CuSO<sub>4</sub>·5 H<sub>2</sub>O, 0.6 g of C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)CH<sub>2</sub>COOK emulsifier and 7.5 g of  
10 (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. The reactor was pressurized with a blend of 61.7 wt% VF<sub>2</sub> and 38.3 wt% HFP to a pressure of 0.83 MPa (120 psig) at 15°C. Agitation (500 rpm) was commenced and a 5 wt% solution of K<sub>2</sub>SO<sub>3</sub> was fed to the reactor. After 30 g of this solution had been added, a drop in  
15 pressure was noted indicating that polymerization was taking place. The monomer mixture was fed to the reactor at a rate to maintain the pressure at 0.83 MPa (120 psig), along with potassium sulfite solution at a rate of 20 g hr<sup>-1</sup>. After 3.5 hours, a total of 1.02 kg  
20 of the monomer mixture had been consumed and a total of 70 g of potassium sulfite solution used. The excess monomer mixture was vented and the reactor drained and the resulting latex coagulated and the white, rubbery polymer product washed and dried as described in Ex. 1.  
25 The polymer had a Mooney viscosity (ML 1+10@ 121°C) of 53 and a composition (by <sup>19</sup>F NMR analysis) of polymer units derived from 61.2 wt% VF<sub>2</sub> and 38.3 wt% HFP and with 0.5 wt% C<sub>8</sub>F<sub>17</sub> end groups.

This example demonstrates that a perfluorinated  
30 radical is formed even in the presence of a competing reducing agent such as potassium sulfite. Thus, the perfluorinated sulfinates of this invention can be used in combination with sulfites and other known reducing agents.

35

### Curing of fluoroelastomers

In the following Examples and Comparative Examples, polymers were cured and tested.

Three of the fluoropolymers of this invention (polymers of Examples 1, 4 and 5), containing perfluoroalkyl end groups, were cured. The cure rheology and cure properties are compared with 5 analogous, Comparative Examples C2, C3 and C4, wherein the fluoropolymers used were prepared with the same monomers but in the absence of fluorochemical sulfinates. The cure compositions and cure rheology and other physical properties are shown in Tables 1 and 10 2 below.

#### Example 10

The fluoroelastomer gum prepared in Example 5 was compounded with 30 phr MT black, 6 phr  $\text{Ca}(\text{OH})_2$ , 3 phr 15  $\text{MgO}$ , and cured with 3.5 millimoles per 100 g of resin (mmhr) bisphenol AF, and 1.27 mmhr of phosphonium cure accelerator,  
[ $(\text{C}_4\text{H}_9)_3\text{P}^+\text{CH}_2\text{CH}(\text{OCH}_3)\text{CH}_3$ ][ $^-\text{OC}_6\text{H}_4\text{C}(\text{CF}_3)_2-\text{C}_6\text{H}_4-\text{OH}$ ] prepared from the reaction of tributyl (2-methoxypropyl) phosphonium 20 chloride and the sodium salt of hexafluoroisopropylidene bis(4-hydroxybenzene).

#### Comparative Example C2

A fluoroelastomer gum was prepared as in Example 5 25 except without  $\text{C}_8\text{F}_{17}\text{SO}_2\text{Na}$ . The resulting gum was cured and tested as in Example 10.

#### Example 11

30 The fluoroelastomer gum of Example 4 was cured and tested as in Example 10 except with 3 phr of  $\text{Ca}(\text{OH})_2$ , 2.5 phr of triallylisocyanurate (TIAC), and 2.5 phr Luperco 101 XL organic peroxide from Atochem, and without  $\text{MgO}$ , bisphenol AF, and phosphonium cure 35 accelerator.

#### Comparative Example C3



A fluoroelastomer gum was prepared as in Example 4 except with 0.4 weight % BDFE and without  $C_4F_9SO_2Na$ . The resulting gum was cured and tested as in Example 11. The polymer contained 0.25 wt. % bromine as determined by X-ray fluorescence.

#### Example 12

The fluoroelastomer gum of Example 1 was cured and tested as in Example 10.

10

#### Comparative Example C4

A fluoroelastomer gum was prepared as in Example 1 except without  $C_8F_{17}SO_2Na$ . The resulting gum was cured and tested as in Example 10.

15

Table 1

Example	C2	10	C3	11	C4	12
Rheology Data Rheometer 177° C, 3° arc, 100 cpm						
$M_L, N.m$	1.13	1.80	2.03	1.24	1.24	1.70
$t_{12}$ (minutes)	2	1.9	1.2	1.4	1.1	1.2
$t_c'$ (50) (minutes)	2.8	2.8	2.3	2.5	1.6	1.8
$t_c'$ (90) (minutes)	3.1	3.1	5.1	5.5	1.8	2.0
$M_H, N.m$	7.91	9.15	8.70	4.75	10.4	10.4
$\Delta$ Torque ( $M_H - M_L$ )	6.78	7.35	6.67	3.51	9.16	8.70

20

25

Table 2

	Cured Properties Press cure 10 min. @ 177°C & post cure 16 hrs @ 230°C						
5	Tensile, MPa	11.9	13.3	16.7	13.4	15.6	16.1
	Elongation, %	270	285	241	336	197	213
	100 % modulus	4.97	4.00	4.08	2.88	5.54	5.29
	Hardness (Shore A2)	80	75	71	68	74	74
	Compression Set						
10	O-rings, 70 hrs @ 200°C	39.5	24.3	34.6	48.1	21.0	20.7
	Heat-aged dumbbells (70 hrs @ 275°C)						
15	Tensile, MPa	4.00	6.93				
	Elongation, %	445	370				
	100 % modulus	2.00	2.03				
	Hardness (Shore A2)	80	72				

20        The data in Tables 1 and 2 show that the polymers  
of this invention are readily cured with either a  
bisphenol (Examples 10 and 11) or a peroxide (Example  
11) cure system, giving good physical properties. In  
particular, Example 10 illustrates (compared with  
25 Comparative Example C2) that cured polymers of this  
invention have improved properties, e.g., compression  
set resistance, and better retention of physical  
properties after heat aging compared to  
fluoroelastomers prepared by conventional methods.

30        Various modifications and alterations of this  
invention will be apparent to those skilled in the art  
without departing from the scope and spirit of this  
invention and this invention should not be restricted  
to that set forth herein for illustrative purposes.

What is Claimed is:

5        1. A method for the preparation of fluorine-  
containing polymer comprising, polymerizing, under  
free-radical conditions, an aqueous emulsion or  
suspension of a polymerizable mixture comprising a  
fluoroaliphatic-radical containing sulfinic acid, and an  
10 oxidizing agent capable of oxidizing said sulfinic acid to  
a sulfonyl radical.

2. The method of claim 1 wherein said oxidizing  
agent is water-soluble and is selected from the group  
15 consisting of sodium, potassium, and ammonium  
persulfates.

3. The method of Claim 1 wherein said sulfinic acid  
is  $R_f(SO_2M_{1/x})_n$  where  $R_f$  is fluoroaliphatic radical, M is a  
20 hydrogen atom or a cation of valence x, and n is 1 or  
2.

4. A fluorine-containing polymer comprising at  
least one mono-, di-, or tri-valent fluoroaliphatic  
25 moiety derived from a fluoroaliphatic sulfinic acid  
salt.

5. The copolymer of claim 9 wherein said  
fluoroaliphatic moiety is selected from the group  
30 consisting of fluoroalkyl groups of formula  $C_nF_{2n+1}$   
wherein n is 3 to 12 and fluoroalkylene groups of  
formula  $C_nF_{2n}$  wherein n is 4 to 12.

6. A polymer comprising the divalent  
fluoroaliphatic moiety

5



or the divalent fluoroaliphatic moiety

$-\text{CF}_2\text{O}(\text{C}_2\text{F}_4\text{O})_m(\text{CF}_2\text{O})_n\text{CF}_2-$ , wherein m and n are 1 to 20.

10

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 5 C08F14/18

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,21 04 077 (DAIKIN KOGYO CO., LTD) 5 August 1971 ---	1
A	DE,A,27 39 282 (KURARAY CO., LTD) 2 March 1978 ---	1
A	EP,A,0 048 308 (ASAHI GLASS CO., LTD) 31 March 1982 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

15 April 1994

Date of mailing of the international search report

04. 05. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

Glikman, J-F

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-2104077	05-08-71	GB-A- 1316222	09-05-73
DE-A-2739282	02-03-78	JP-C- 1177219	14-11-83
		JP-A- 53030193	22-03-78
		JP-B- 56033363	03-08-81
		JP-A- 53039331	11-04-78
		FR-A,B 2363613	31-03-78
		GB-A- 1567670	21-05-80
		US-A- 4182035	08-01-80
EP-A-0048308	31-03-82	NONE	